THE REACTION BETWEEN OXYGEN AND 2-BUTENE

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INTRODUCTION

At the present time the mechanism of the gaseous oxidation of hydrocarbons is in dispute. During the latter half of the 19th century some investigators held that in the combustion of hydrocarbons the hydrogen is preferentially burned. In opposition to this was the claim that the carbon is preferentially burned. In 1902 Bone[1] proved that there is no preferential burning of either carbon or hydrogen and advanced the idea that the oxidation of hydrocarbons proceeds through hydroxylation. Ethene when oxidized was found by Bone and Wheeler[2] to yield small amounts of acetaldehyde in addition to carbon oxides, water and other secondary reaction products. The acetaldehyde was postulated as being formed by rearrangement of vinyl alcohol, the primary reaction product.

$$\underset{\text{ethene}}{CH_2{=}CH_2} \xrightarrow{O} \underset{\text{vinyl alcohol}}{CH_2{=}CHOH} \longrightarrow \underset{\text{acetaldehyde}}{CH_3{-}CHO}$$

Vinyl alcohol is known to rapidly and quantitatively isomerize to acetaldehyde. Bone and other investigators[3a-f] have presented much additional evidence in favor of the hydroxylation theory of oxidation of hydrocarbons.

Some recent investigations, however, have indicated that oxidation proceeds through the formation of a primary peroxide, this peroxide then reacting with additional hydrocarbon molecules or else decomposing to yield the final reaction products. Thus Callendar and Mardles[4] propose the primary reaction of oxygen with methane to be

as follows:

$$\underset{\text{methane}}{CH_4} + O_2 \longrightarrow \underset{\text{methyl hydrogen peroxide}}{CH_3OOH}$$

Recent work on ethene[5a,b,c], propene[5d], pentenes[5e], cyclo-hexene[5f], and styrene[5g] has indicated that the reaction products of oxidation can be most satisfactorily accounted for by assuming the reaction to be initiated by the formation of an active or "dative" peroxide.

It was thought that the oxidation of 2-butene under conditions which would enable the isolation of the primary oxidation products would throw some light on the mechanism of gaseous oxidations in general. Accordingly a study has been made of the oxidation of 2-butene using a short time of contact in the heated reaction zone and an amount of oxygen much less than required for complete combustion.

EXPERIMENTAL

Materials: The 2-butene was prepared by heating 100 ml. n-butanol (Eastman no. 50) with 100 ml. 95% C.P. sulfuric acid and 50 ml. water in a 1-liter, 3-neck flask. The butene is purified by passing through a spiral reflux condenser, through three spiral wash bottles, the first two of which contain 40% by volume of sulfuric acid to remove alcohol vapors while the third contains 40% potassium hydroxide solution to remove any traces of sulfur dioxide, through a tower half filled with soda lime and half with calcium chloride, and is condensed in a trap immersed in a freezing mixture. Young and Lucas[6] have shown that butene so prepared consists entirely of cis- and trans-2-butene.

Apparatus: The oxidation apparatus is shown in figure 1. A to H consists of a device for delivering gas at a constant rate. Various other apparatus were tried and found to be unsatisfactory. The apparatus here described was found to be very satisfactory in that a constant, non-fluctuating flow was quickly and easily obtainable.

ABC is a 14 mm. tube projecting about 100 cm. above the top of the five-gallon bottle, D. At the point B, the tube ABC is constricted by a 5-cm. length of 1 mm. internal diameter capillary tubing. Just below this capillary tube, the tube ABC has a pinhole, PH, which allows the pressures to be equal in the bottle and in the tube ABC below the capillary. E is a 6-mm. tube extending to the bottom of the bottle. F is a 6-mm. delivery tube. G is a calcium chloride tower. H is a sensitive needle valve.

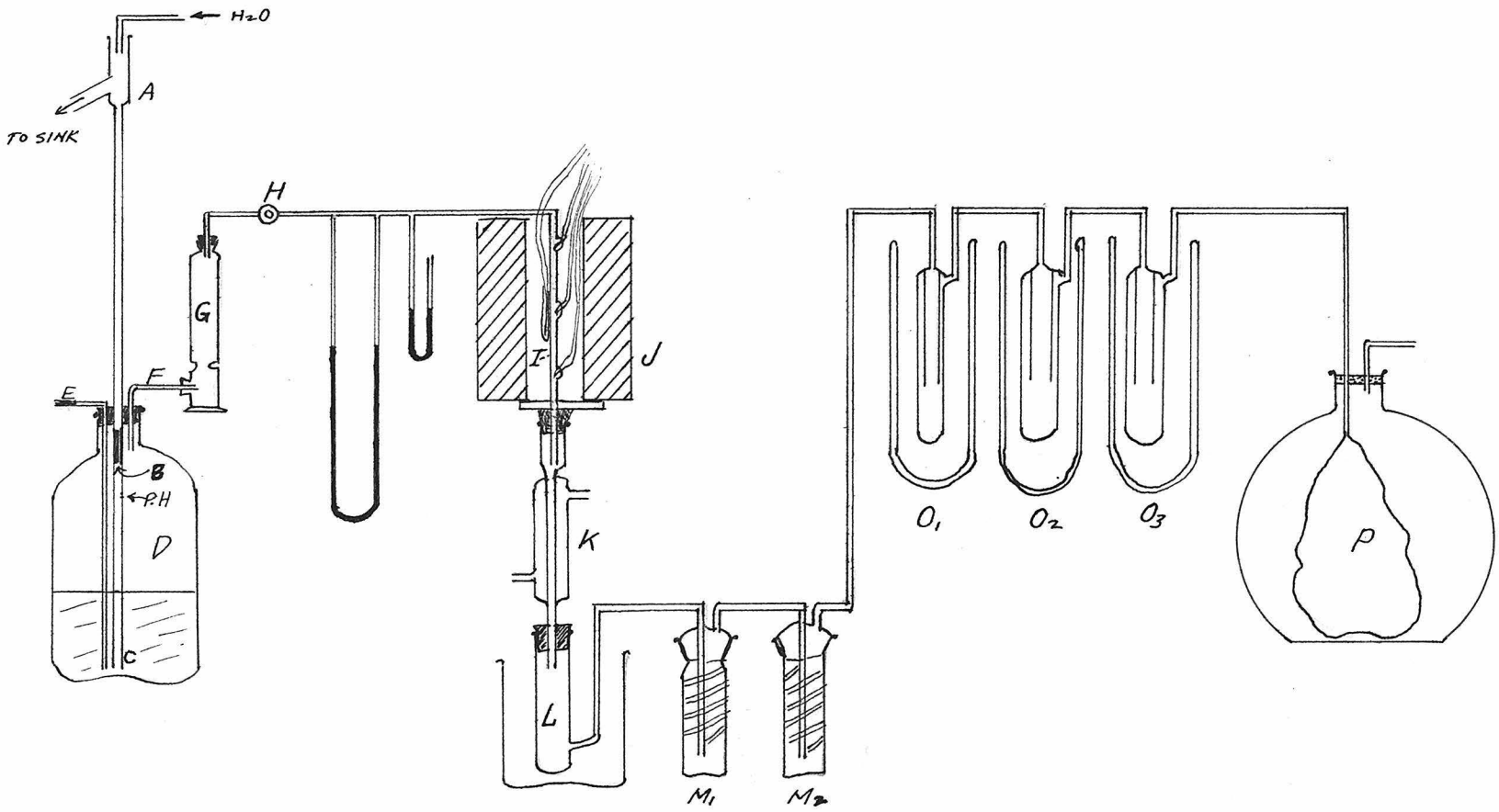


Figure 1

To use the apparatus, water is run into A, most of which overflows to the sink. Tube AC fills up, with water flowing through the capillary B into D under an effective head of water equal to the distance AB, 100 cm. The needle valve, H, is kept closed until the pressure in D builds up to 100 cm. water when the back pressure just balances the column of water AB. At this point water stops flowing into bottle D. Then the needle valve, H, is opened and adjusted to give the desired rate of flow. The portion BC of tube ABC prevents excessive washing of the butene mixture by the falling stream of water.

After leaving the needle valve, the gas mixture passes through a flowmeter and into the reaction tube, I, heated in an electric furnace, J. The reacted gases are cooled by a condenser, K, and ice trap L. The cooled gases pass through two water-filled spiral wash-bottles M_1 and M_2 to remove water-soluble reaction products, through trap O_1 cooled in an ice-hydrochloric acid mixture, and then through two traps, O_2 and O_3, cooled in solid carbon dioxide-alcohol mixture. The uncondensed gases are collected in the rubber balloon, P.

The reaction tube consists of a 7-mm. ID pyrex tube, 30 cm. of which is inside the furnace. Temperatures inside the reaction tube are measured by three chromel-alumel thermocouples fused in the reaction tube at equal intervals. The furnace temperature was measured by an additional thermocouple located alongside the reaction tube. A Leeds and Northrup student type potentiometer was used to measure the thermal electromotive force. The temperature of the reaction tube is taken as that indicated by the thermocouple in the middle of the reaction tube.

The flowmeter was calibrated by passing a butene-oxygen mixture through it at a definite measured rate. It was found that the

indicated rate of flow of the butene-oxygen mixture through the flowmeter calibrated with air was 35% lower than the actual rate. For this reason it was necessary to recalibrate the flowmeter using a butene-oxygen mixture of the same composition as the mixture used in the experiments.

Before starting an oxidation, butene was volatilized into a 5-gallon bottle displacing brine. Oxygen was added in the desired amounts from a cylinder and the mixture allowed to stand overnight to insure thorough mixing. This gas mixture was then driven into the bottle D just before an oxidation was started.

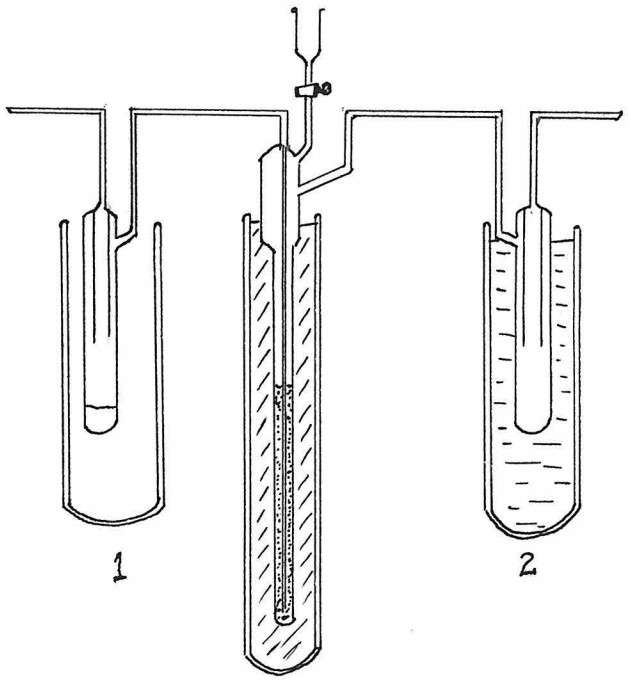
During an experiment the gases were passed through the furnace at an average rate of 62.2 ml. per minute, with a contact time of 11 seconds. The oxidations were continued for about three hours in order to collect appreciable amounts of the reaction products. Immediately after completion of an experiment the exhaust gases were transferred from the balloon to a glass flask and stored over mercury.

ANALYSIS OF REACTION PRODUCTS

Gas Samples: The samples of the entering gas were analyzed in an Orsat apparatus. The exhaust gases were analyzed by a combination of an Orsat analysis and a distillation analysis through a Podbielniak column[7]. Unfortunately the latter results will not be available for a short time. The available results are incorporated in Table II.

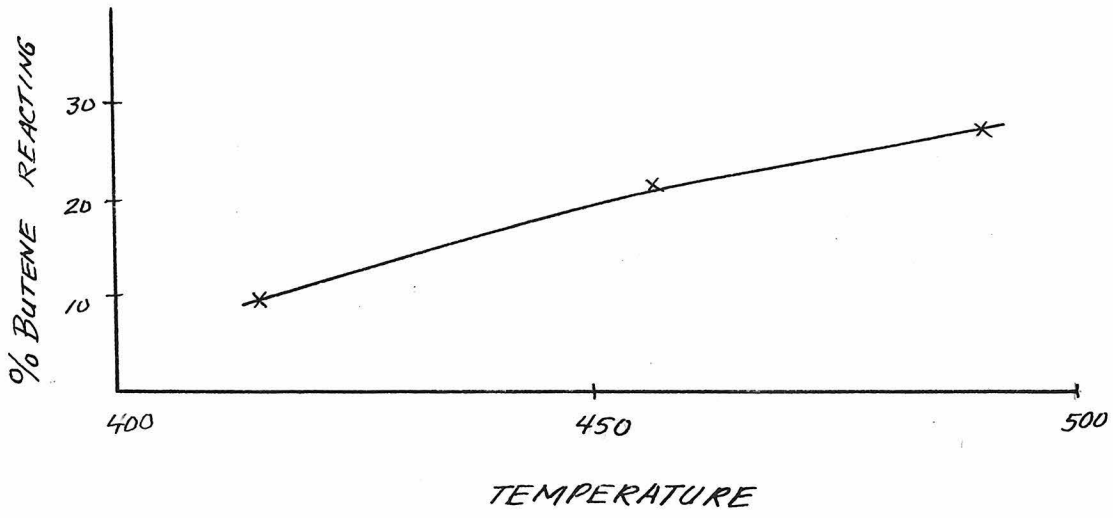
Condensates in Traps O_1, O_2, and O_3: The condensates in these traps consisted almost entirely of butadiene and unreacted butene. These were converted into the corresponding tetra- and di-bromides by distilling the condensates through a column of bromine kept in the dark and at a temperature only slightly above the freezing point of the brominating mixture. The apparatus used for this conversion is shown in figure 2.

Figure 2



The condensate is volatilized from trap 1, through the column of bromine into trap 2. One passage through the bromine gives practically complete absorption. Some bromine vapors pass into trap 2 and there react with any unreacted condensate. The bromine used was purified by washing with saturated potassium bromide solution and then distilling from concentrated sulfuric acid. The brominated condensates were washed with an excess of sodium bisulfite solution, washed well with sodium bicarbonate solution, washed with water, dried over calcium chloride, and distilled through a vacuum jacketed Vigreux column designed by Weston[8]. The residue in the flask crystallized on cooling and was the tetrabromide of 1,3-butadiene. This was established by its melting point and by a mixed melting point with known butadiene tetrabromide. The distillate consisted of dibromobutanes. By subtracting the amount of butene recovered as dibromobutane from the amount of butene passed, the amount of butene reacting was found. The results are best shown in figure 3 in which the percent of butene reacting per mole of butene passed is plotted against the temperature.

Figure 3



At temperatures below 400° very little reaction takes place. At temperatures above 500° soot is formed indicating that secondary reactions are occurring. This amount of butene reacting is not necessarily a measure of the primary reaction as butene may be involved in secondary reactions. More will be said of this later.

Wash Waters: Total aldehyde was determined in the wash waters by a gravimetric determination of the total weight of dinitrophenylhydrazones which were obtained from an aliquot of the wash water on adding an excess of dinitrophenylhydrazine. This method is based on the assumption that the aldehyde is all present as acetaldehyde. Actually acetaldehyde constituted at least 90% of all aldehydes present.

The analysis of the carbonyl compounds was effected by identification of the 2,4-dinitrophenylhydrazones prepared after the method of Brady[9]. An aliquot of the precipitated hydrazones was fractionally extracted and crystallized by means of alcohol. The derivatives were separated into two components: (a) a relatively insoluble osazone of glyoxal (or glycollic aldehyde) and (b) a less insoluble hydrazone of acetaldehyde. It is not possible by this method to distinguish between glyoxal and glycollic aldehyde as both yield the same osazone. It was impossible to isolate any 2,4-dinitrophenylhydrazone of the following: formaldehyde, propionaldehyde, n- or iso-butyraldehydes, crotonic aldehyde or methylethylketone.

In calculating the composition of the original hydrazone and osazone mixture it was assumed to consist of only derivatives of acetaldehyde and glyoxal and that the recovery of the glyoxal osazone was quantitative. To facilitate the identification of the reaction products

the dinitrophenylhydrazones of the following compounds were prepared. The derivatives are listed in Table I along with the melting points, color and crystalline form.

TABLE I. 2,4-DINITROPHENYLHYDRAZONES

Compound	Melting Point °Cobs.	Literature Values	Color and crystalline form
formaldehyde	166	155	orange plates
acetaldehyde	150.2	147	yellow powder
propionaldehyde	158	155	brilliant red plates
n-butyraldehyde	120	122	orange needles
iso-butyraldehyde	182	182	orange prisms
acrolein	158.(dec)	165	red powder
crotonaldehyde	187.5	190	fine red crystals
glyoxal*	322.(dec)	318	orange crystals
methyl glyoxal	158.		orange
methyl glyoxal*	250.(dec)		orange
dimethylketone	125.8	128	yellow needles and prisms
methylethylketone	112.5	115	orange needles and plates
methylpropylketone	137.5	141	orange needles
methylcyclo-hexylketone	139.	140	orange
glyoxalic acid	195.	190	red plates
pyruvic acid	197.5	213	yellow needles

* osazone

The n- and iso-butyraldehydes were prepared by oxidation of n- and iso-butyl alcohols with chromic acid. The glyoxal was prepared by oxidation of ethene with selenium dioxide according to the method of Riley and Friend[10]. The methylcyclohexylketone was prepared by chromic acid oxidation of methylcyclohexyl carbinol. This carbinol was prepared by adding acetaldehyde to cyclohexylmagnesium bromide and decomposing the addition compound with water. The other carbonyl compounds were purified from samples obtained from the supply room.

In connection with the use of 2,4-dinitrophenylhydrazine as a reagent for carbonyl compounds it was noticed that the ordinarily available reagent consisted of a mixture of yellow and red crystals when viewed under the microscope. Under proper conditions it was possible to make the sybstance crystallize out in either the yellow or the red form, depending upon the solvent used. It was further noticed that the yellow apparently changed over to the red form when heated. Report of this phenomenon has not been located in the literature and may warrant further investigation.

The acid in the wash waters was determined by titration with standard sodium hydroxide solution using phenolphthalein as an indicator.

Peroxide was tested for qualitatively with titanium tetrachloride in 6-normal hydrochloric acid[11].

CONDENSATE IN ICE TRAP

The condensate in the ice trap varied from a few drops at the lower temperature up to 8.9 ml. at the higher temperature per mole of butene passed. At temperatures above 450°, the condensate consisted of two phases; the upper phase was an oil of density less than one. Both phases had very penetrating odors, gave positive tests for peroxide, good iodoform tests, and reacted acid to litmus.

The molecular weight of the oil phase was determined by reacting a portion with standard bromide-bromate solution in the presence of excess acid. Assuming one double bond per molecule the molecular weight of the oil was found to be 124 - 125. The value for octene is 112. Evidently the oil phase is impure octene formed by the polymerization of two molecules of butene.

RESULTS AND DISCUSSION OF RESULTS

The experimental data and results of the analyses are shown in Tables II and III.

TABLE II

Experimental Data and Analysis of Condensates

Temp. °C	Ave. rate of flow ml/min	Length of exp. min.	Entering Gas % C_4H_8	% O_2	% N_2	C_4H_8 passed moles	Dibromobutane isolated gms.	moles	Tetrabrombutane isolated gms.	moles	Remarks
415	62.3	185	55.2	40.1	4.7	0.2650	51.6	0.2390	1.4	0.00380	) Flow fluctuated
456	59.3	199	53.6	39.4	7.0	0.2660	43.3	0.2080	1.9	0.00509	) due to poor gas) delivery device.
490	65.0	192	56.4	41.4	2.2	0.2925	46.4	0.2152	3.5	0.00937	Flow very constant Used device described

TABLE III

Analysis of Wash Waters and Ice-trap Condensate

Temp. °C	Ice-trap cond. Oil ml	Water ml	Mol. Wt. Oil	2,4-dinitrophenylhydrazones Total moles	Approx. Percent acetald.	glyoxal	Acid Equiv.	Peroxide Qualitative Test	Iodoform Test
415		0.1		0.0127	97-98	3-2	+	-	+
456	0.3	1.2	125.0	0.0379	88-92	12-8	0.00118	+	+
490	0.9	1.7	124.2	0.0438	95-97	5-3	0.000164	+	+

These results, recalculated on the basis of moles of products formed per mole of butene passed are shown in Table IV.

TABLE IV

Moles Product per Mole Butene Passed

Temp. °C	Ice-trap cond. Oil ml	Water ml	Butene reacting moles	Butadiene formed moles	Total aldehyde moles	Acid equivalents
415		0.4	0.098	0.0159	0.0480	+
456	1.1	4.5	0.218	0.0191	0.1425	0.00445
490	3.1	5.8	0.265	0.0321	0.1496	0.00056

These results are in general agreement with the corrected results of Ross Morris[12]. Unfortunately the original calculations are in error due to a large error in the flowmeter calibrations. Using Morris' original data and applying the correct flowmeter readings the results in Table V are obtained. The experimental conditions were the same in both cases.

TABLE V

Moles Product per Mole Butene Passed

Temp. °C	Total aldehyde moles	Acid equiv.	Olefin oxide moles	Peroxide equiv.
375	0.0356	+	+	
391	0.0366	+	+	+
418	0.082	0.0204	0.000805	+
421	0.084	0.0130	0.00388	0.00956
447	0.1620	0.0214	+	+
472	0.1396	0.00525	0.000732	0.00613
485	0.1055	0.00430	0.0	0.00583

Morris also observed that the aqueous phase of the condensate gave a positive test for formic acid when heated with powdered mercuric oxide.

The results of the oxidation may be explained in a variety of ways. If the initial reaction is one of hydroxylation two products might be expected. They are the enol form of methylethylketone, $CH_3-CH=CHOH-CH_3$, and crotyl alcohol, $CH_3-CH=CH-CH_2OH$. If the enol form of methylethylketone were formed it would immediately isomerize into the keto form. This was not found among the reaction products. According to Pope, Dykstra and Edgar[13], oxidation of hydrocarbons proceeds by an attack at the end of the chain. If this occurs, crotyl alcohol might be formed. Crotyl alcohol at the high temperatures might undergo an allylic rearrangement to yield methylvinylcarbinol.

$$\underset{\text{crotyl alcohol}}{CH_3-CH=CH-CH_2OH} \longrightarrow \underset{\text{methylvinylcarbinol}}{CH_3-CHOH-CH=CH_2}$$

This rearrangement seems entirely likely as bromine derivatives of similar compounds are known to undergo allylic rearrangements at temperatures much lower than those attained in the oxidation apparatus. If methylvinylcarbinol were formed it might lose water and form 1,3-butadiene.

$$\underset{\text{methylvinylcarbinol}}{CH_3\text{-}CHOH\text{-}CH_2\text{=}CH_2} \longrightarrow \underset{\text{1,3-butadiene}}{CH_2\text{=}CH\text{-}CH\text{=}CH_2} + H_2O$$

The presence of crotyl alcohol and methylvinylcarbinol has not as yet been established in the reaction products. Butadiene, however, has been found to be present at all temperatures studied. Its presence is best explained through the pyrolysis of methylvinylcarbinol produced as explained above. Butadiene might conceivably be formed from the elimination of water between a molecule of 1-butene and oxygen, the 1-butene being formed through rearrangement of 2-butene. If, however, considerable amounts of 1-butene were formed, formaldehyde and propionaldehyde would be expected to be among the products. Neither of these were found. It is probable, however, that any formaldehyde formed would be immediately decomposed. Bone[14] reports that formaldehyde is rapidly decomposed above 400° while Bone and Stocking[15] report that other aldehydes are decomposed at much lower temperatures according to the reaction:

$$CH_3CHO \longrightarrow CH_4 + CO.$$

Some formaldehyde is undoubtedly formed in this reaction from the oxidation of butadiene as glyoxal and/or glycollic aldehyde is formed. This can best be explained by the following reaction:

$$\underset{\text{butadiene}}{CH_2\text{=}CH\text{-}CH\text{=}CH_2} + 2O_2 \longrightarrow \underset{\text{glyoxal}}{CHO\text{-}CHO} + \underset{\text{formaldehyde}}{2HCHO}$$

It is possible that this reaction proceeds through an intermediate peroxide.

While the formation of butadiene can be best explained on the basis of hydroxylation, the main oxidation reaction, the formation of acetaldehyde, can be best explained on the basis of peroxide formation. The peroxide would be formed from a molecule of butene and one of oxygen as follows:

$$CH_3\text{-}CH{=}CH\text{-}CH_3 + O_2 \longrightarrow CH_3\text{-}CH(O_2)\text{-}CH\text{-}CH_3$$

2-butene — 2-butene peroxide

This peroxide then might react in a variety of ways. The main reaction is the thermal decomposition into acetaldehyde.

$$CH_3\text{-}CH(O_2)\text{-}CH\text{-}CH_3 \longrightarrow 2\ CH_3CHO$$

while a second reaction might involve an unreacted butene molecule to yield butene oxide:

$$CH_3\text{-}CH(O_2)\text{-}CH\text{-}CH_3 + CH_3\text{-}CH{=}CH\text{-}CH_3 \longrightarrow 2\ CH_3\text{-}CH(O)\text{-}CH\text{-}CH_3$$

butene oxide

If this reaction occurs some of the butene is then disappearing in a secondary reaction and the amount of butene used up is not a criterion of the amount of primary reaction occurring.

The peroxide might also react with water to form hydrogen peroxide and butene oxide:

$$CH_3\text{-}CH(O_2)\text{-}CH\text{-}CH_3 + H_2O \longrightarrow CH_3\text{-}CH(O)\text{-}CH\text{-}CH_3 + H_2O_2$$

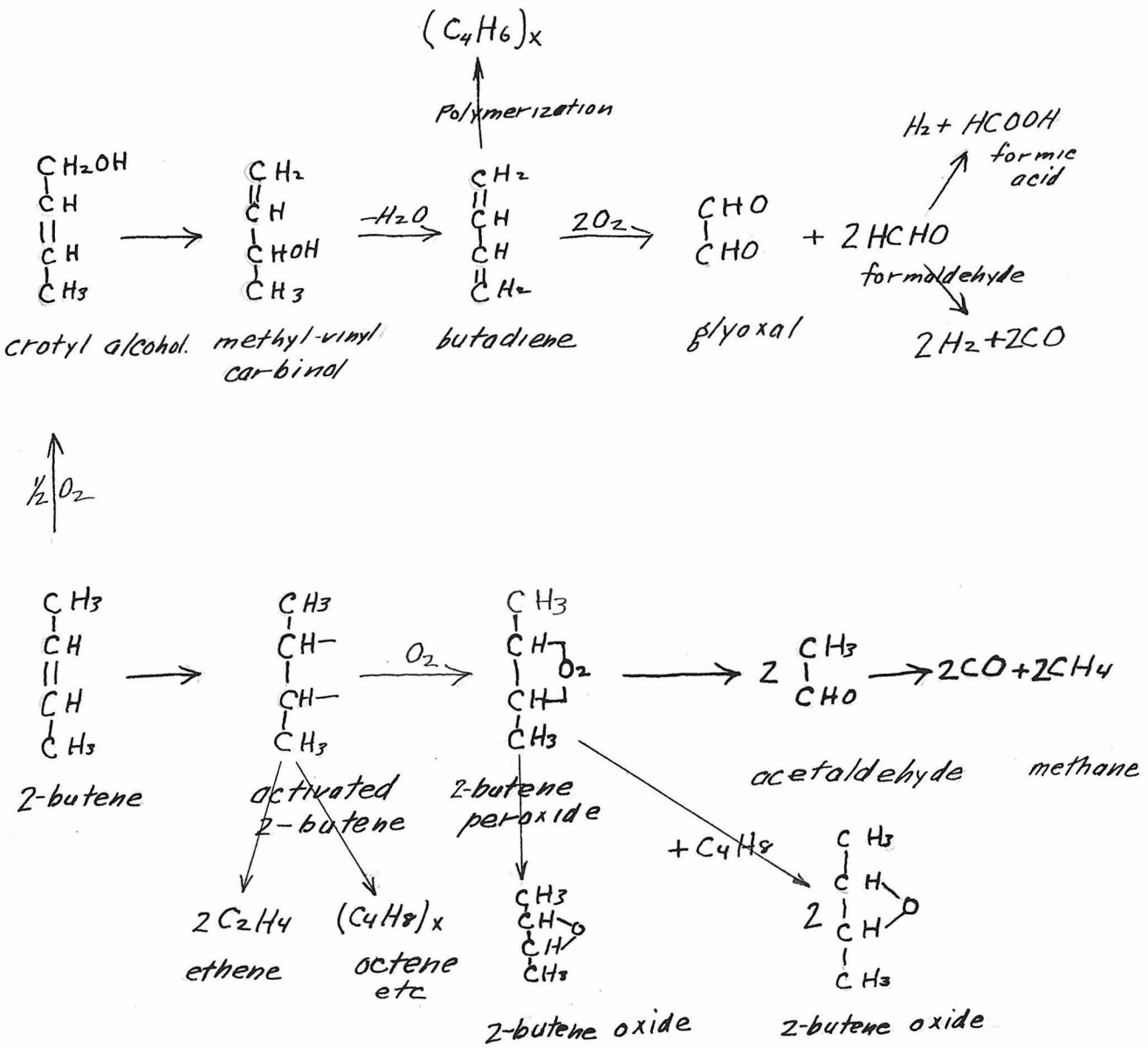
Any hydrogen peroxide so formed might react with aldehydes to give hydrogen, saturated hydrocarbons and acids as Fry and Payne[16] have shown that formaldehyde reacts with hydrogen peroxide in the presence of sulfuric acid to give hydrogen and formic acid, while paraldehyde reacts to give formic and acetic acids and methane.

The amount of polymerization occurring is no doubt more than would have occurred if oxygen were absent as Engler[17] found that oxygen markedly increased the rate of formation of polymers from olefines and dienes.

As accurate analyses of the exhaust gases are not yet available, it is not possible to state at this time the extent to which the butene suffers pyrolysis.

The results are diagrammatically shown in Chart 1.

Chart 1



SUMMARY

2-Butene has been found to react with oxygen at temperatures of 375° to 500°. At the higher temperatures, polymerization as well as oxidation takes place. The products of the reaction which have been identified are acetaldehyde, glyoxal and/or glycollic aldehyde, 1,3-butadiene, acid, peroxide and an olefin oxide[12]. The simplest explanation of the reactions occurring involve both hydroxylation and peroxide formation as primary products.

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